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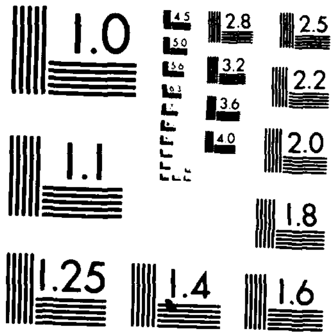

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MULTIREFERENCE CI GRADIENTS AND MCSCF SECOND DERIVATIVES

Byron H. Lengsfield, III
Paul J. Saxe
George F. Adams
Michael J. Page

May 1986

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*Los Alamos National Laboratory, Los Alamos, NM 87545
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A set of simple and efficient formulas for the calculation of multireference CI gradients and MCSCF second derivatives is presented. The CI gradient formalism is extended to include a general class of references in the CI. This extension is necessary for the calculation of gradients for a commonly employed class of CI wavefunctions for which the reference configurations are selected from a generalized CAS MCSCF wavefunction. In addition, we report the first general multireference CI gradient calculations. The

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calculations are for the reaction Be + H_2 → BeH_2 constrained to C_{2v} symmetry. Structures of the reactant and transition state and the activation energy calculated at the selected reference CI level compare favorably to the full second order CI results. MCSCF second derivatives are found to be useful for the optimization of the CI structures.

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I. INTRODUCTION

Recent advances in the efficient evaluation of integral derivatives[1-3] have resulted in a renewed interest in the analytical evaluation of the first and second derivatives of the energy with respect to nuclear coordinates for Hartree-Fock and post-Hartree-Fock wavefunctions. Much of this work has been pioneered by Pople and co-workers[4,5] who developed efficient codes both for the evaluation of the second derivatives of the integrals and for solving the coupled-perturbed Hartree-Fock equations. The first and second derivatives are extremely useful tools for optimizing structures, characterizing stationary points, and calculating vibrational frequencies, as well as for more extensive studies of the Born-Oppenheimer potential energy surface away from the stationary points. The last several years have also seen tremendous advances made in CI[6-10] and MCSCF[11-27] methodologies, which coupled with the interest in derivatives, have led to powerful techniques for a wide range of wavefunctions. In this vein, we report our work on general, multireference CI gradients and MCSCF second derivatives.

Before presenting our work, it is appropriate to quickly review the previous activity in the area of CI gradients and MCSCF second derivatives. In 1980, both Krishnan, et al.[5] and Brooks, et al.[28] presented both equations and algorithms for the analytical computation of single-reference UHF or closed-shell RHF CI gradients. Osamura, et al. extended the capabilities to include open-shell RHF reference functions,[29] and more recently published the equations for general multireference CI gradients.[30] Yamaguchi, et al.[31] reported second derivatives for two-configuration SCF (TCSCF) wavefunctions and Camp, et al.[32] developed the methodology and implemented second derivatives for CAS MCSCF wavefunctions. Independently, Pulay,[33] as well as Jorgensen and Simons,[34] have provided equations for MCSCF second derivatives. The work on both multireference CI gradients and MCSCF second derivatives is closely related since a major step in both types of calculation is the solution of the coupled-perturbed MCSCF (CPMCSCF) equations.

In this paper we report the first general multireference CI gradient calculations. We have extended the theory developed by Osamura, et al.[30] to include a general class of references in the CI. This extension is necessary for the calculation of gradients for a commonly employed class of CI wavefunctions for which the reference configurations are selected from a generalized CAS MCSCF wavefunction. By generalized CAS we mean that there is at least one partially occupied orbital subspace where the energy is invariant to rotations of the orbitals in space. The simplest example of this type of wavefunction is a full CI in a selected subspace of orbitals. The length of the CI expansion in such a calculation grows rapidly with the size of the active space. To avoid unreasonably large MCSCF expansions, it is desirable to partition the space of chemically active orbitals and perform CAS calculations in some or all of the subspaces, while a GVB type wavefunction might be used in the remaining subspaces. A MCSCF calculation where all single and double excitations are generated from one subspace into another subspace would also be considered a generalized CAS wavefunction. In order to calculate the gradient of a selected reference CI wavefunction in which the orbitals are obtained from a generalized CAS wavefunction, orbital derivatives not appearing in the CPMCSCF equations are needed and we develop the machinery necessary to obtain these quantities.

We also present the equations employed in our MCSCF second derivative calculations. Our equations are an extension of the open-shell SCF second derivative formulas of Osamura, et al.[42] These equations are different from those presentedy by Pulay[33] and Jorgensen and Simons[34] principally in the manner in which the derivative overlap contributions are handled. We expand upon these differences later in the text. In addition, the open-shell second derivative formulas of Osamura, et al.[42] are reformulated so that we need not contract Coulomb or exchange operators after the CPMCSCF equations are solved.

The CPMCSCF equations are also presented in a more compact and convenient manner than Osamura's. The gradient-like terms appearing in the CPMSCF are defined in terms of modified integrals involving derivative overlap terms, as well as integrals involving derivative atomic orbitals. This formulation is particularly convenient when MCSCF second derivatives are desired.

Finally, we present the results of sample calculations on the reaction, $Be + H_2 \rightarrow BeH_2$. Here, second derivatives obtained at the MCSCF level are used in the optimization of the geometry of the products and for locating the transition state at the multireference CI level. We compare the results obtained at the second-order CI level with the results obtained in a selected reference CI (SRCI) calculation.

II. COMPUTATIONAL DETAILS

A. First Derivatives

The energy of a general CI wavefunction

$$\Psi = \sum_i C_i X_i \tag{1}$$

can be expressed as

$$E = \sum_{ij} \left(\sum_{p,q} C_p K^{ij}_{pq} C_q \right) h_{ij} + \sum_{ijkl} \left(\sum_{p,q} C_p K^{ijkl}_{pq} C_q \right) g_{ijkl} \tag{2a}$$

$$= \sum_{ij} D_{ij} h_{ij} + \sum_{ijkl} D_{ijkl} g_{ijkl} \tag{2b}$$

$$= \sum_{p,q} C_p H_{pq} C_q \ , \tag{2c}$$

where C is the CI vector, X is a configuration state function (CSF), h_{ij} and g_{ijkl} are one and two electron MO integrals, K^{ij}_{pq} and K^{ijkl}_{pq} are spin coupling constants, and H_{pq} is an element of the Hamiltonian matrix in our CSF basis. D_{ij} and D_{ijkl} are one-particle and two-particle density matrix elements, respectively. The first derivative of the CI energy, with respect to nuclear coordinates, is[28]

$$E^a = \sum_{pq} C_p H^a_{pq} C_q + \sum_{i}^{occ} \sum_{r}^{all} L_{ri} U^a_{ri} \tag{3a}$$

$$= \sum_{ij} D_{ij} h^a_{ij} + \sum_{ijkl} D_{ijkl} g^a_{ijkl} + \sum_{i}^{occ} \sum_{r}^{all} L_{ri} U^a_{ri} \tag{3b}$$

In this equation h^a_{ij} and g^a_{ijkl} are derivatives of the one- and two-electron atomic orbital integrals transformed to the molecular orbital basis. The derivatives of the molecular orbital expansion coefficients corresponding to orbital i, ϕ^a_i, are expressed in terms of undifferentiated coefficient vectors ϕ_p as

$$\phi^a_i = \sum_p U^a_{pi} \phi_p \tag{4}$$

L_{ri} is a Lagrangian multiplier defined as

$$L_{ri} = 2 \left(\sum_j D_{ij} h_{rj} + 2 \sum_{jkl} D_{ijkl} g_{rjkl} \right) \tag{5}$$

For a MCSCF wavefunction

$$L_{ij} = L_{ji} \text{ for ij occupied} \tag{6a}$$

and

$$L_{ri} = 0 \text{ for i = occupied and r = virtual.} \tag{6b}$$

These relations are simply a reflection of the variational conditions on the orbitals. Not all of the elements of U^a_{ij} are independent. By differentiating the orthonormality condition

$$U^+ S U = I \tag{7}$$

one obtains

$$U^a_{ij} + S^a_{ij} + U^a_{ji} = 0, \tag{8}$$

where

$$S^a_{ij} = \sum_{xy} \phi_{xi} \; S^a_{xy} \; \phi_{yj} \; . \tag{9}$$

S^a_{xy} is the derivative of the x,y atomic orbital overlap integral with respect to nuclear coordinate a. U^a_{ij} can then be expressed as a sum of an antisymmetric matrix and an upper triangular matrix

$$U^a_{ij} = \Delta^a_{ij} + T^a_{ij}, \tag{10}$$

where

$$\Delta^a_{ij} = -(\Delta^a_{ij})^+ \tag{11}$$

and T^a_{ij} is defined by

$$T^a_{ij} = -S^a_{ij} \text{ for } i<j \tag{12a}$$

$$= -\frac{1}{2} S_{ii} \text{ for } i=j \tag{12b}$$

$$= 0 \text{ for } i>j \quad . \tag{12c}$$

Thus, the derivative of the MCSCF energy is

$$E^a = \sum_{ij} D_{ij} h^a_{ij} + \sum_{ijkl} D_{ijkl} g^a_{ijkl} + \sum_i^{occ} \sum_j^{all} L_{ij} T^a_{ij} \tag{13}$$

since

$$\sum_i^{occ} \sum_r^{all} L_{ri} \Delta^a_{ri} = 0 \quad . \tag{14}$$

Before proceeding with a discussion of the CPMCSCF equations, it is useful to further examine the contributions to the first derivative. We note that it is possible to rewrite the first derivative for a CI wavefunction as

$$E^a = \sum_{pq} C_p H^a_{pq} C_q + \sum_{pq} C_p H^{U^a}_{pq} C_q \quad . \tag{15}$$

This equation is obtained by reordering the sums in Eq. (3a) as follows:

$$\sum_i^{occ} \sum_r^{all} L_{ri} U^a_{ri} = \sum_i \sum_j D_{ij} (\sum_r 2 U^a_{ri} h_{rj})$$

$$+ \sum_{ijkl} D_{ijkl} (\sum_r 4 U^a_{ri} g_{rjkl}) \tag{16a}$$

$$= \sum_i D_{ij} \sum_r (U^a_{ri} h_{rj} + U^a_{rj} h_{ri}) \tag{16b}$$

$$+ \sum_{ijkl} D_{ijkl} \sum_r (U^a_{ri} g_{rjkl} + U^a_{rj} g_{irkl}$$

$$+ U^a_{rk} g_{ijrl} + U^a_{rl} g_{ijkr})$$

$$= \sum_{ij} D_{ij} h^{U^a}_{ij} + \sum_{ijkl} D_{ijkl} g^{U^a}_{ijkl} \tag{16c}$$

$$= \sum_{p,q} C_p H^{U^a}_{pq} C_q \quad , \tag{16d}$$

where

$$h^{U^a}_{ij} = \sum_r (U^a_{ri} h_{rj} + U^a_{rj} h_{ri}) \tag{16e}$$

and

$$g^{U^a}_{ijkl} = \sum_r (U^a_{ri} g_{rjkl} + U^a_{rj} g_{irkl} + U^a_{rk} g_{ijrl} + U^a_{rl} g_{ijkr})$$

Similarly, the first derivative of the MCSCF energy is

$$E^a = \sum_p \sum_q C_p H^a_{pq} C_q + \sum_p \sum_q C_p H^{T^a}_{pq} C_q \quad . \tag{17}$$

Partial-derivative integrals similar to $h^{U^a}_{ij}$ and $g^{U^a}_{ijkl}$ arise naturally in the quadratic SCF procedure of Bacskay[35] and in the atomic orbital based CPHF equations of Osamura, et al.[36] They have also been exploited by Olsen, et al.[23] in a cubic MCSCF procedure and by Lengsfield[22] in a quadratic MCSCF approach designed to handle large CI expansions. These integrals have also been used by Dupuis,[37] Pulay,[33] and Jorgensen and Simons[34] to simplify their derivative expressions. The partial-derivative Hamiltonian constructed from these quantities is particularly useful as it occurs in both the CPMCSCF equations and in the expressions for the MCSCF second derivatives.

B. Coupled Perturbed MCSCF Equations

The derivative of the molecular orbitals U^a_{ij}, which are needed to compute the CI gradient, are obtained by solving the CPMCSCF equations. These equations are generated by requiring that the wavefunction satisfy the MCSCF variational conditions to first order with a change in nuclear geometry. Thus, these equations result from requiring that the derivatives of the orbital and CI stationary conditions, with respect to a nuclear coordinate, vanish.

$$\frac{dG_{ij}}{da} = \frac{d(L_{ij}-L_{ji})}{da} = 0 \tag{18a}$$

$$= \frac{\partial G_{ij}}{\partial a} + \sum_{mn}{}' \frac{\partial \Delta_{mn}}{\partial a} \frac{\partial G_{ij}}{\partial \Delta_{mn}} + \sum_p \frac{\partial C_p}{\partial a} \frac{\partial G_{ij}}{\partial C_p} + \sum_s^{occ} \sum_r^{all} \frac{\partial T_{rs}}{\partial a} \frac{\partial G_{ij}}{\partial T_{rs}} \tag{18b}$$

and

$$\frac{dG_p^{CI}}{da} = \frac{d}{da}\sum_q (H_{pq} - E\delta_{pq})\, C_q = 0 \tag{19a}$$

$$= \frac{\partial G_p^{CI}}{\partial a} + \sum_{mn}{}' \frac{\partial \Delta_{mn}}{\partial a}\frac{\partial G_p^{CI}}{\partial \Delta_{mn}} + \sum_q \frac{\partial C_q}{\partial a}\frac{\partial G_p^{CI}}{\partial C_q} + \sum_s^{occ}\sum_r^{all} \frac{\partial T_{rs}}{\partial a}\frac{\partial G_p^{CI}}{\partial T_{rs}} \quad . \tag{19b}$$

The prime sign indicates that the sum only runs over the unique orbital rotations which change the energy. Gathering the terms which are known on the right-hand side of the equation, we obtain the CPMCSCF equations

$$\sum_{mn}{}' \left(\frac{\partial G_{ij}}{\partial \Delta_{mn}}\right) \Delta_{mn}^a + \sum_q \left(\frac{\partial G_{ij}}{\partial C_q}\right) C_q^a = -\,(G_{ij}^a + G_{ij}^{T^a}) \ , \tag{20}$$

$$\sum_{mn}{}' \left(\frac{\partial G_p^{CI}}{\partial \Delta_{mn}}\right) \Delta_{mn}^a + \sum_q \left(\frac{\partial G_p^{CI}}{\partial C_q}\right) C_q^a = -\,[(G_p^{CI})^a + (G_p^{CI})^{T^a}] \quad , \tag{21}$$

where

$$\Delta_{mn}^a = \frac{\partial \Delta_{mn}}{\partial a} \text{ and } C_q^a = \frac{\partial C_q}{\partial a} \ ,$$

with the condition that

$$\sum_p \frac{\partial C_p}{\partial a} C_p = 0 \quad .$$

In these expressions the superscript "a" in G_{ij}^a and $(G_p^{CI})^a$ is used to denote that derivative AO integrals are employed in the construction of these quantities. The left-hand side of these equations contains explicitly the Hessian matrix appearing in second order MCSCF theory. These equations are in fact similar in structure to the second order MCSCF equations, and can thus be most efficiently solved by expressing the CI variations in the CSF basis, as noted by Lengsfield and Liu.[21,22] These equations are also similar to those obtained by Osamura, et al.[30] However, we have reordered the sums appearing on the right-hand side of this equation in order that the quantities needed to compute the MCSCF second derivatives are readily available.

C. MCSCF Second Derivatives

The derivative with respect to a nuclear displacement can be expanded as follows:

$$\frac{d}{db} = \left(\frac{\partial}{\partial b} + \sum_r^{all}\sum_i^{all} \frac{\partial U_{ri}}{\partial b}\frac{\partial}{\partial U_{ri}}\right) + \sum_p \frac{\partial C_p}{\partial b}\frac{\partial}{\partial C_p} \tag{22a}$$

$$= \left(\frac{\partial}{\partial b} + \sum_r^{all} \sum_i^{all} U^b_{ri} \frac{\partial}{\partial U_{ri}}\right) + \sum_p C^b_p \frac{\partial}{\partial C_p} \quad . \tag{22b}$$

The second derivative of our MCSCF wavefunction is obtained by applying this operator to our expression for the first derivative. It simplifies matters if we make use of both expressions (Eqs. (13) and (15)) for the first derivative. Our second derivative expression is obtained by operating on Eq. (13) with the first two terms in Eq. (22) and then operating on Eq. (15) with the last term in Eq. (22).

We obtain

$$E^{ab} = 2 \sum_{pq} C^b_p H^a_{pq} C_q + 2 \sum_{pq} C^b_p H^{T^a}_{pq} C_q + \sum_{ij} D_{ij} h^{ab}_{ij} + \sum_{ijkl} D_{ijkl} g^{ab}_{ijkl}$$

$$+ \sum_i^{occ} \sum_r^{all} L^a_{ri} U^b_{ri} + \sum_i^{occ} \sum_r^{all} L^b_{ri} T^a_{ri} + \sum_i^{occ} \sum_r^{all} L^{U^b}_{ri} T^a_{ri} \tag{23}$$

$$+ \sum_{ij}^{occ} L_{ij} T^{ab}_{ij} + \sum_{ij}^{occ} L_{ij} \left(\sum_m^{all} U^b_{mi} T^a_{mj} + T^a_{im} U^b_{mj}\right) \quad .$$

Note that only the first two terms are unique to MCSCF second derivatives. The remaining terms are equivalent to the open-shell formulas of Osamura, et al.[42] It is also important to note that almost all of the quantities involving MO or CI derivatives are generated by setting up or solving the CPMCSCF equations. In particular, the vector

$$B^a_p = \sum_q (H^a_{pq} + H^{T^a}_{pq}) C_q$$

can be stored when $G^a_{CI} + G^{T^a}_{CI}$ is constructed. Moreover, the Lagrangian multipliers L^a_{ri} and $L^{T^a}_{ri}$ are used to obtain the gradient terms G^a_{ij} and $G^{T^a}_{ij}$ in the CPMCSCF equations. The trace of the density matrix with the second derivative integrals is calculated by transforming the density matrix elements to the AO basis. The most time consuming step in this transformation only requires mn^4 multiplications where m is the number of active orbitals and n is number of basis functions. The remaining contributions can be obtained from the product of one-particle density matrices.

The only term which requires further consideration is $\Sigma_{ir} L^{U^b}_{ri} T^a_{ri}$. This term formally requires one to contract Coulomb and exchange operators (or more efficiently to contract Osamura's Y_{nimj} matrix) with the solution to the CPMCSCF equations, U^b, to form $L^{U^b}_{ri}$. However, we can eliminate this step by noting that

$$\sum_r^{all} \sum_i^{occ} L_{ri}^{U^b} T_{ri}^a = \sum_r^{all} \sum_i^{occ} L_{ri} T_{ri}^a U_{ri}^b$$

$$+ \sum_{ij}^{occ} L_{ji} \sum_p^{all} (U_{rp}^b T_{pi}^a - T_{rp}^a U_{pi}^b) \quad . \tag{24}$$

The right-hand side of this equation is particularly convenient as all of these terms are generated when we set up the CPMCSCF equations. Using this relation and Eq. (10), we now obtain the final second derivative expression.

$$E^{ab} = 2 \sum_{pq} C_p^b (H_{pq}^a + H_{pq}^{T^a}) C_q + \sum_{ij} D_{ij} h_{ij}^{ab} + \sum_{ijkl} D_{ijkl} g_{ijkl}^{ab}$$

$$+ \sum_r^{all} \sum_i^{occ} L_{ri}^b T_{ri}^a + \sum_r^{all} \sum_i^{occ} (L_{ri}^a + L_{ri}^{T^a}) U_{ri}^b \tag{25}$$

$$+ \sum_{ji}^{occ} L_{ji} [T_{ji}^{ab} + \sum_p^{all} (T_{pi}^a T_{pj}^b + T_{pi}^a T_{jp}^b)] \quad .$$

Equation (23) can be decomposed in another fashion if the orthonormality conditions are expressed in such a way that T is symmetric. Camp, King, McIver, and Mullally[32] have expressed the orthonormality conditions in this way. However, there is an advantage in employing an upper triangular T matrix as only the first p (p is the number of occupied orbitals) columns are needed to obtain the integrals $h_{ij}^{T^a}$ and $g_{ijkl}^{T^a}$. Thus, the transformations needed to obtain $h_{ij}^{T^a}$ and $g_{ijkl}^{T^a}$ can be performed very efficiently. This fact is also exploited in Osamura's equations.

D. Selected Reference CI Gradients

The gradient of the energy for a CI wavefunction requires knowledge of the first order variations in the molecular orbitals. The CPMCSCF scheme does not uniquely define a tranformation of the orbitals, but only specifies a transformation of the variational parameters. This is enough information to define an orbital transformation excluding an arbitrary orthogonal mixing within the invariant subspaces. If the CI wavefunction has the same invariant subspaces as the reference wavefunction, then the gradient is well defined. This is the case, e.g., with a SDCI using closed-shell Hartree-Fock orbitals. Both wavefunctions are invariant to mixings among the doubly occupied core orbitals and information concerning such mixings is not required for the CI gradient.

For a CI wavefunction constructed as all excitations of a given order from selected references of a generalized CAS wavefunction, this is not the case. The CI is not invariant to mixings of orbitals within the partially

occupied subspaces. The most common way to address this problem in calculating the CI energy itself is to require that the orbitals be natural orbitals of the one-particle density matrix. For the calculation of the CI gradient, we then remove the ambiguity by requiring the natural orbital conditions to be satisfied to first order with a change in nuclear geometry. The derivative of the natural orbital condition must vanish in analogy with Eqs. (18) and (19) for the variational conditions.

$$\frac{d}{da}(DW - W\lambda) = 0 \quad . \tag{26}$$

Here D is a subblock of the one particle density matrix and λ is a diagonal matrix of occupation numbers. At a=0, W=I, and thus $D(0)=\lambda(0)$.

Evaluating Eq. (26) leads to expressions for the derivatives of parameters which mix orbitals within the invariant subspace.

$$\Delta^a_{ij} = W^a_{ij} = \frac{-D^a_{ij}}{\lambda_i - \lambda_j} \quad . \tag{27}$$

In this equation, $D^a_{ij} = 2\,\Sigma_{pq}\, C^a_p K^{ij}_{pq} D_q$ and C^a_p is obtained from the solution to the CPMCSCF equations. Δ^a_{ij} is then obtained with the overlap derivative portion T^a_{ij} as in Eq. (10) to obtain U^a_{ij}.

III. COMPARISON WITH OTHER WORK

As noted in the Introduction, our second derivative expressions differ from those of Pulay[33] and Jorgensen and Simons[34] principally in the manner in which the derivative overlap terms are included in the CPMCSCF equations, and subsequently in the final expression for the second derivatives. Jorgensen and Simons include an overlap term in the definition of their AO basis. They are then able to derive a very compact set of formulas. However, the formulas for the derivatives of their AO integrals are involved and the overall efficiency of their method depends very strongly on how their derivative AOs are computed. We should also note that Jorgensen and Simons' method was developed to describe second derivatives of CI and coupled-cluster wavefunctions, as well as MCSCF wavefunctions. The comparative efficiency of their method must also be judged on how well it treats highly correlated wavefunctions, and this analysis is beyond the scope of the present study.

Pulay has derived the CPMCSCF equations in such a manner that the orbital variations are expressed in the AO basis (as opposed to the MO basis used by Osamura) and the CI variations are in the CSF basis. His CPMCSCF equations do not require a contraction of Coulomb and and exchange operators with overlap terms, but his CPMCSCF equations are larger than Osamura's because he is working in the AO basis. We feel that the overall efficiency of both methods should be about the same. However, we also note that Pulay's equations neglect projection operator terms appearing in Osamura's equations (see also Lengsfield and Liu[21]). These terms are needed if the Hessian appearing in the CPMCSCF equations is to be nonsingular.

The recent communication by Camp, et al.,[32] provides few details of their second derivative equations. However, they express the variation of the molecular orbitals with nuclear displacement in terms of a product of an exponential and a Hermitian operator. The orthonormality conditions at first order are treated by this Hermitian operator as opposed to the upper triangular matrix appearing in Eq. (12). Further details are needed to determine if the simplicity of their final equations offset the computational expense of working with a Hermitian matrix as opposed to an upper triangular matrix in constructing terms like L^{T^a} appearing in our second derivative expression.

IV. SAMPLE CALCULATIONS

The reaction $Be + H_2 \rightarrow BeH_2$ was studied in C_{2v} symmetry. The geometry of the products and transition state was stabilized at the MCSCF and multi-reference CI level. The MCSCF wavefunction employed in this study was a four-electron in four-orbital CAS. This wavefunction correctly describes the cleavage of the BeH bonds, but does not contain all of the configurations needed to describe s^2 and p^2 near degeneracy in Be. Second order CI calculations, based on the 4 in 4 CAS, are compared to the results of selected reference singles and doubles CI (SRCI) calculations. In the SRCI calculations, the references were selected on the basis of their cumulative weight in the natural orbital representation of the MCSCF wavefunction. The weight, W, was defined as follows:

$$W = \sum_i C_i^2 \quad . \tag{28}$$

The basis set used for beryllium was Dunning's 5s contraction[38] of Huzinaga's 10s primitive set[39] and Bartlett's p function[40] composed of three primitives which we augmented with an uncontracted p function of exponent 0.057 181. The hydrogen basis was Dunning's 2s contraction[41] of Huzinaga's 4s primitive set[39] with a scale factor of 1.2. The results of these calculations are presented in the following four tables. Table 1 lists the references employed in the SRCI calculations. The stable geometries are given in Table 2, and the MCSCF vibrational frequencies in Table 3. Our calculated MCSCF and CI energies are given in Table 4.

The reaction is symmetry forbidden along the C_{2v} reaction path and this results in a transition state with two dominant CSFs.

The results of the SRCI calculations accurately reproduce the second order CI results while only requiring a fraction of the computational effort. The MCSCF calculations provide a good description of the reaction (in this basis) but the activation energy is a bit high as expected.

We found that the multireference CI gradient calculations converged very rapidly to stable points when MCSCF second derivatives and starting geometries were employed. In the most unfavorable case, four iterations were required for convergence (largest component of the gradient less than 1.0×10^{-4} a.u./bohr).

Table 1. Dominant Configurations in the MCSCF Wavefunction

Equilibrium Geometry Configuration		Coefficient
1	$1a_1^2 2a_1^2 1b_2^2$	0.989
2	$1a_1^2 2a_1 1b_2 3a_1 2b_2$	0.092

Weight = 0.98766

Transition State Geometry Configuration		Coefficient
1	$1a_1^2 2a_1^2 1b_2^2$	0.740
2	$1a_1^2 2a_1^2 3a_1^2$	-0.623
3	$1a_1^2 2a_1 1b_2 3a_1 2b_2$*	-0.197 0.117

*The two coefficients associated with this configuration correspond to the two spin couplings.

Table 2. Geometries of BeH_2 Stationary Points

	MCSCF	SRCI	SDCI
Equilibrium			
R_{BeH}	2.61 876 bohr	2.60 512 bohr	2.60 637 bohr
Θ	180.00°	180.00°	180.00°
C_{2v}	3.0875 bohr	3.0687 bohr	3.0693 bohr
Θ	47.38°	48.68°	48.76°

Table 3. MCSCF Vibrational Frequencies

Equilibrium	Transition State
790.1 cm^{-1}	4044.9i cm^{-1}
790.1 cm^{-1}	
1827.5 cm^{-1}	993.4 cm^{-1}
2069.4 cm^{-1}	4514.7 cm^{-1}

Table 4. MCSCF and CI Energies for BeH_2

	MCSCF	SRCI	SDCI
Equilibrium	-15.773 651 a.u.	-15.798 597 a.u.	-15.798 965 a.u.
Transition State	-15.597 013 a.u.	-15.628 925 a.u.	-15.629 315 a.u.
ΔE	0.176 638 a.u. (110.8 kcal)	0.169 672 a.u. (106.5 kcal)	0.169 650 a.u. (106.45 kcal)

V. CONCLUSION

We have presented a set of simple and efficient formulas for the calculation of multireference CI gradients and MCSCF second derivatives. The additional machinery needed to compute selected-reference CI gradients was developed. Sample calculations were presented in which SRCI structures and activation energies compared very favorably with the full second order CI results. In the reaction investigated in this work, MCSCF second derivatives were found to be very useful in the stabilization of the CI structures.

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